PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number:
D21C 3/02, C12P 7/10 C12S 3/02	A1	WO 90/10748
		(43) International Publication Date: 20 September 1990 (20.09.90)

(21) International Application Number: PCT/SE90/00169

(22) International Filing Date: 16 March 1990 (16.03.90)

(30) Priority data:
8900940-1 16 March 1989 (16.03.89) SE

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(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
In English translation (filed in Swedish).

(54) Title: PREPARATION OF CELLULOSE AND FERMENTATION OR NUTRIENT PRODUCTS FROM THE BIOMASS OF WHOLE ANNUAL PLANTS, PREFERABLY CEREALS

(57) Abstract

The present invention relates to a process for the manufacture of a cellulose-containing product, whereby the whole biomass from annual cellulose-producing plants, particularly cereals, is treated with alkali.

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PREPARATION OF CELLULOSE AND FERMENTATION OR NUTRIENT PRODUCTS FROM THE BIOMASS OF WHOLE ANNUAL PLANTS, PREFERABLY CEREALS.

DESCRIPTION

Technical filed

The raw material of today for the preparation of cellulose for paper production is primarily wood pulp. A number of processes are used. They are characterized most of all of high investment costs and a high energy consumption due to high process temperatures with a high working pressure, which results in troublesome discharges to air, land and water recipients.

As a complement to the more and more decreasing supply of wood raw material other cellulose sources, such as energy forests, grass, straw, leguminous plants etc. been tested. In general one has then used the same production technique as used for wood pulp and thereby obtained the same end results upon the environment.

The present invention relates to a reduction of the environmental problems described as well as energy costs by working with another raw material, running the process at a low temperature, a low pressure and a small consumption of chemicals.

As cellulose raw materials annual cereals are primarily used, such as wheat, rye, barley, etc. but also rice, corn, reed, grass and leguminous plants.

In the process the whole biomass is used. The whole biomass of for example wheat, rye, barley can be divided into a straw part (the straw with its stem, leaves and husks) and a grain part (the grain with the core). The straw part is then present as main raw material for the cellulose recovery. The grain part as a main component for the recovery of a nutrient solution, alternatively for the fermentation of alcohols. The embodiment of the invention is described in the flow diagram of appendix 1 and 2.

In the description below the nomenclature "cellulose" is used as a collective name for a number of components of the composition of the biomass. At the combination of straw and grain for the recovery of cellulose as well as a nutrient solution, and alcohol, alternatively, thus the husk fraction is part of this name. The composition of the raw materials is evident from the appendix 3.

The process is controlled by addition of alkali, temperature, and reaction time. As alkali known hydroxides of primarily Na and Ca are used, alone or in combination. In particular $Ca(OH)_2$ has turned out to be favourable at the returning to the farming land. Purification and recovery of Na, respectively can be made in any method known from the cellulose technique. The temperature can be varied within wide limits from 20°C to close to the boiling point, 95°C. The reaction time is dependent on the addition of alkali and temperature. The process is controlled and run using known technique from the cellulose industry.

The following notifications are used in the examples given below:
pH is determined electrometrically direct in a test sample of the slurry at 20°C, Ac is determined as used, and added alkali, respectively. 10 g of filtrated slurry is diluted to about 100 ml and is titrated using 1/10 N HCl to pH 8.5 (phenolphtaleine). The amount of 1/10N HCl used is = acidity. rTS is determined refractometrically using a ABBE refractrometer for the sugar industry., °Brix is connected to refraction index and gives directly %TS (dry matter contents) in a sugar solution.

The raw material consists of field harvested crop whole biomass of wheat consisting of 50 % by weight of straw mass and 50 % by weight of grain mass. The variation is normally ±10%. In order to obtain internally reproducible laboratory samples field harvested biomass has been threshed and fractionated in a pure straw part and a pure grain part. The fractions are then used together in the weight relationship 50:50. Grinding of the

fractions has been made on a hammer mill using 2 mm sieve openings.

Embodiment examples.

Example 1.

Relates to the processing of the whole biomass to cellulose part (solid part), and nutrient solution (liquid part) comprising the straw as well as the insoluble nutrients of the grain part which have been converted enzymatically to soluble compounds such as glucose, proteins and salts. Flow diagram in appendixes 1 and 2.

Process: 300 g of biomass (150 g of straw and 150 g of grain part) are ground into 3000 g of water. The pH of the slurry is adjusted to pH about 7 using calcium hydroxide solution. Then 0.25 g of alfa-amylase, Termamyl^{R}, 0.25 g of a protease, Neutrase^{R}, and 0.5 g of a combination enzyme SP 342 comprising cellulase, gluconase, hemicellulae and protease are added. All the enzymes are manufactured by NOVO, Copenhagen, DK. The slurry is heated to 50 ^{o}C for 2 hrs. The temperature is raised to 95^{o}C for 1 hr and is then cooled to 65^{o}C. pH is adjusted to about 4.5 using 4 g of phosphoric acid. Then 0.4 g of amyloglucosidase (NOVO) are added. The solution is being completely saccharified for 16 hrs, whereupon the enzymes present are inactivated by raising the temperature to 95^{o}C. The slurry is cooled and is separated into one solid and one liquid phase in a screen centrifuge. The solid phase, the fibres, are washed with water. Yield 2,200 g of liquid phase having a 5% DS and 2,200 g of washing solution having a 0.3% DS (return solution for the next production cycle). Yield of syrup: 2,200 g x 5,3 DS. Yield of fibres: 580 g of moist material from the straw and grain parts, which is fed to the cellulose/paperproduction. The amount of fibre obtained, 580 g, is fed into 2,200 g of water and 40 g of $Ca(OH)_2$. Analysis of the process liquid: rTS = 1,0, pH = 12.1, Ac = 24. The slurry is kept at 90-95^{o}C for about 6 hrs, the a stabilization of the pH and Ac have been obtained. The slurry is adjusted to the original 3,170 g. Analysis: rTS = 1.6, pH = 11.7, Ac = 9.5. Solid and liquid phases are separated in a

screen centrifuge. The fibres are washed using water, and the wash water is returned to a new cycle together with the process liquid having been separated off. The alkali-fibres having been washed are ground using 2 l of water, are neutralized to pH 6.5 using phosphoric acid. The slurry is diluted to 5 l. The pulp is drawn off on a wire cloth and is washed. The cake is dried for 12 hrs at 75°C. Yield: 126 g DS paper pulp. To obtain a higher end concentration of the nutrient solution (5.0% DS) the amount of biomass 300 g can be complemented with a further 150 g of wheat grain only. Hereby an increase of of about 10% nutrient solution is obtained. To another 150 g of wheat grains, i.e. to a total of 450 g of wheat grains, an about 15% nutrient solution is obtained simultaneously as the yield of cellulose increases due to the husk fraction of the wheat grains.

Example 2.

Relates to processing of the whole biomass to paper and alcohol.

Flow diagram appendixes 1 and 2.

Process: 300 g of biomass (150 g of straw part, and 150 g of grain part) are fed into 3000 g of water, pH is adjusted to about 7 using some calcium hydroxide solution. Subsequently 0.25 g of alfa-amylase, Termamyl^{R}, and 0.25 g of protease, Neutrase^{R}, were added. The slurry was heated to 50°C for 0.5 hrs. Then the temperature was raised to 95°C for 1 hr. The slurry was then cooled to 65°C and the slurry was adjusted to 3.300 g, and pH was lowered to 4.5 using 4 g of phosphoric acid, whereupon 0.5 g of amyloglucosidase, NOVO, were added. Complete saccharification of the sugar part for 16 hrs, whereupon the enzymes were deactivated at 95°C for 0.5 hrs. The slurry was cooled to 35°C and fermented at 35°C for 18 hrs when the release of CO_2 ceased. From the mash thus obtained 500 g of a distillate containing 10.3% ethanol was distilled off, which gives 51.5 g of 100 % ethanol. The slurry remaining in the fermentation and distillation column was diluted to 3.300 g. Solid and liquid phases were separated using a screen centrifuge. The fibres were washed using 300 g of water. Yield: 602 g of moist

fibres. These fibres were fed down into 2000 g of water + 15 g of NaOH. The analysis of the process liquid: rTS = 1.4, pH = 11.9; Ac = 21. The slurry was kept at 20 to 22°C for 12 hrs when a stabilization had been obtained. Analysis of the slurry: rTS = 2.5; pH = 11.4; Ac = 6.6. Solid and liquid phases were separated in a screen centrifuge. The fibres were washed using 300 g of water. Yield: Wet fibres 600 g = 128 g DS in the form of paper pulp, which consists of two cellulose components, the composition of which is evident from appendix 3, Raw materials. The process liquid and the wash water are returned to a new cycle.

In order to determine the contribution of the single components in the yield of alcohol, and cellulose-paper, respectively, of the end product a separate processing of wheat grains only, and straw only, respectively been made according to the following.

Example A

150 g of wheat grains only were processed in accordance with Example 2 above and were fermented whereby 43.9 g of 100 % ethanol were obtained. The remaining slurry was screened and the husk fraction was washed, dried for 12 hrs at 75°C, which gave 14 g DS. The dried husks were soaked into 200 g of water and were processed to paper in accordance with Example 2. Yield: 10 g of cellulose.

Example B

150 g of straw only, were processed in accordance with Example 2 above, whereby 7.4 g of 100 % ethanol were obtained. The remaining slurry of straw was separated off, washed, and subsequently processed to paper, whereby 116 g of cellulose were obtained.

In total: Alcohol: 43.9 + 7.4 = 51.3 g
Cellulose: 10 + 116 = 126 g

Example 3.

Relates to comparative processing of whole biomass to paper and alcohol, where the combination enzyme SP 342 is present. 300 g of biomass are fed into 3000 g of water, pH is adjusted to about 7 using some calcium hydroxide solution. Then 0.25 g of alfa-amylase, Termamyl^{R}, 0.25 g of a protease, Neutrase^{R}, and 0.5 g of SP 342 comprising cellulase, hemicellulase, gluconase, and protease are added. The slurry is heated to 50 °C for 2 hrs, whereupon the temperature is raised to 95°C for 1 hr and is then cooled to 65°C. The weight is adjusted to 3,300 g and pH is adjusted to 4.5 using 4 g of phosphoric acid. Then 0.4 g of amyloglucosidase are added and complete saccharification took place for 16 hrs. The slurry contained 3,177 g having a rTS = 5.2. The slurry was cooled to 35°C, bakery yeast was added and fermentation took place for 18 hrs when the release of CO_2 ceased. From the mash 500 g of an alcoholic solution containing 11.22% by weight of ethanol = 56 g of 100 % ethanol was distilled off. The slurry remaining in the vessel was diluted to 3.000 g and was separated in a screen centrifuge. The fibres were washed, whereby 2500 g of a return solution were obtained for a new cycle, and 574 g of moist fibres. These fibres were fed down into 2000 g of water + 15 g of NaOH. The analysis of the process liquid: rTS = 1.3, pH = 11.8; Ac = 20. The slurry was kept at 20 to 22°C for 12 hrs when a stabilization had been obtained. Analysis of the slurry: rTS = 2.4; pH = 11.4; Ac = 6.5. Solid and liquid phases were separated. The fibres were washed, whereby 565 g of moist fibres and 2300 g of return liquid were obtained having a rTS = 2.1 for a new cycle. The fibres were ground with 2000 g of water and were neutralized using 5 g of phosphoric acid to pH 6.5. The slurry was diluted to 5 l and was drained on a wire screen. The cake was washed. The sheet was dried for 12 hrs at 75°C. Yield: 117 g of cel-lulose-paper pulp DS.

Storage test with preserved biomass using $Ca(OH)_2$

Test material: Totally harvested cut biomass of wheat (harvested during mild rain). The amount of calcium oxide powder was calculated on the DS of the biomass.

Test:

The whole biomass consisted of 50% by weight of straw, and 50 % by weight of grain. Water content 31%. 100 g of biomass were placed in tight plastic bags and calcium oxide powder was added and mixed into it as a pulverulent skin. The bags were flattened and well closed. 3 samples of each mixture were stored in a dark heating cabinet at the temperatures given.

Sample % CaO	Temperature °C	Mildew after 1 months	6 months	12 months
0	20	weak	strong	very strong
1		none	none	weak
2		none	none	none
5		none	none	none
0	37	weak	strong	very strong
1		weak	strong	very strong
2		none	none	none
5		none	none	none

Paper sheets produced from pulp according to the Examples above were tested.

Preparation: The fibre pulp was diluted to about 1.75 g pulp DS/litre of water. So much slurry was used that the final sheet weighed (surface weight) 100 g/m^2. Draining on the wire screen in a sheet former, pressing, drying and conditioning.

The results of the test are evident from the table below:

Table

	Test				
Parameters	1	2	3	4	5
Surface weight g/m^2	100	99	99	98	103
Tensile index Nm/g	40	39	41	40	41
Ductile yield %	1.7	1.8	1.2	1.8	2.0
Burst index Pam^2/g	2.1	2.0	2.2	2.1	2.3
Opacity (60 g/m^2)	99.4	99.2	99.1	99.3	98.3
% Na	<0.1	0.60	0.55	1.0	<0.1
% Ca	3.03	0.13	0.15	0.20	<0.1

Test 1: Nutrient solution + paper with $Ca(OH)_2$
Test 2: Alcohol + paper with NaOH
Test 3: Alcohol with SP 342 + paper with NaOH
Test 4: Straw only + paper with NaOH
Test 5: Preparation of return paper fibres from wood cellulose from paper mill

CLAIMS

1. Process for the preparation of cellulose containing product, characterized by an alkaline treatment of whole biomass from annual cellulose producing plants, preferably cereals.

2. Process according to claim 1, characterized in that the alkaline treatment takes place at a low alkalinity, pH 11.5-13.5 and at a temperature of 20 to 95°C.

3. Process according to claims 1-2, characterized in that one or more of NaOH, $Ca(OH)_2$, KOH andNH_3 are used as an alkaline source.

4. Process according to claims 1-3, characterized in that an enzymatical treatment takes place prior to a subsequent fermentation to alcohol or isolation of a nutrient solution at the processing of whole biomass.

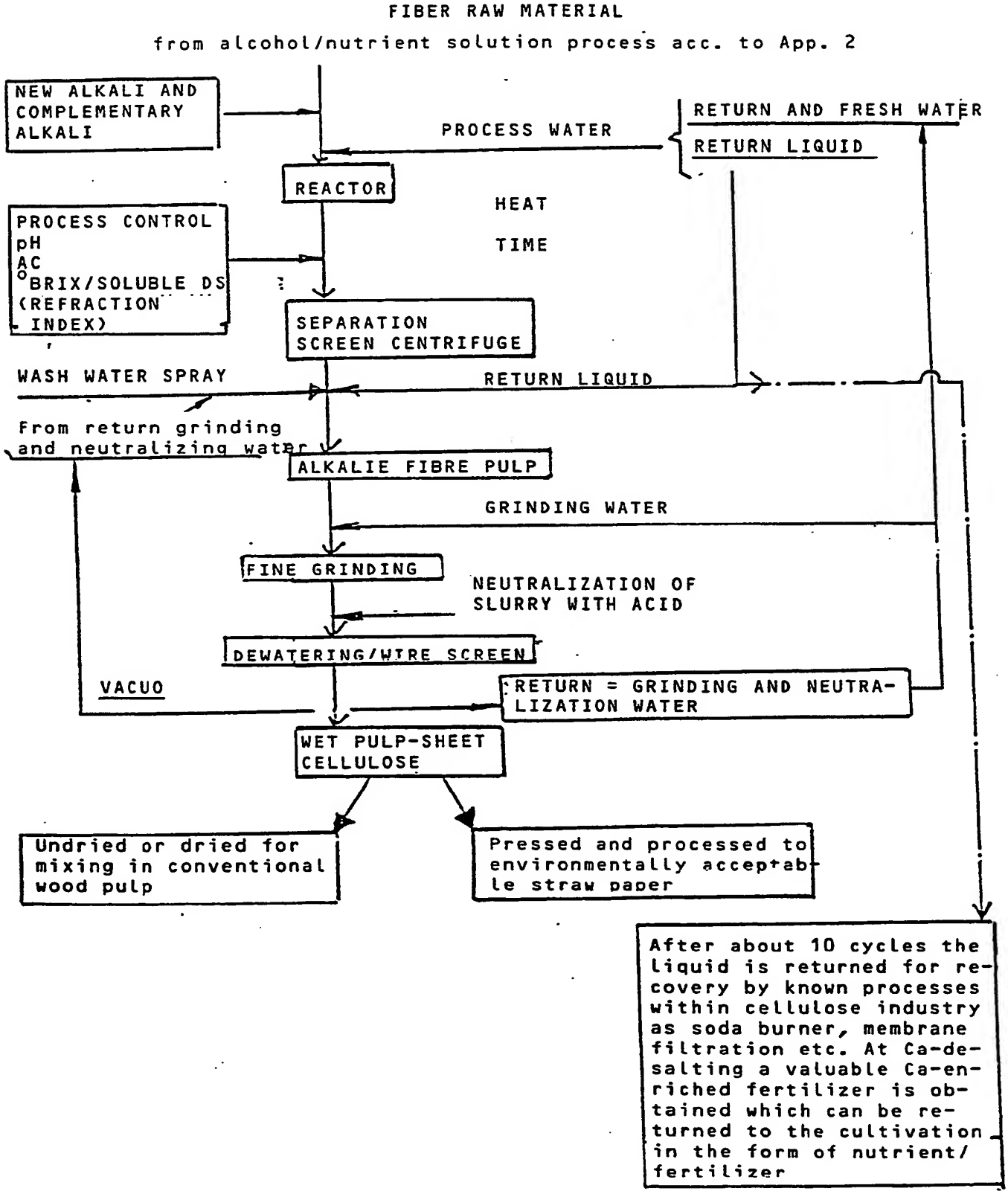
5. Process according to claim 4, characterized in that the biomass is enzymatically treated with alfa-amylase, amyloglucosidase, protease, and optionally a combined enzyme comprising cellulase, hemicellulase, gluconase and protease.

6. Process according to claims 1-3, characterized in that the alkaline treatment of the cellulose content takes place subsequent to the distillation of fermented alcohol, or recovery of nutrient solution, respectively.

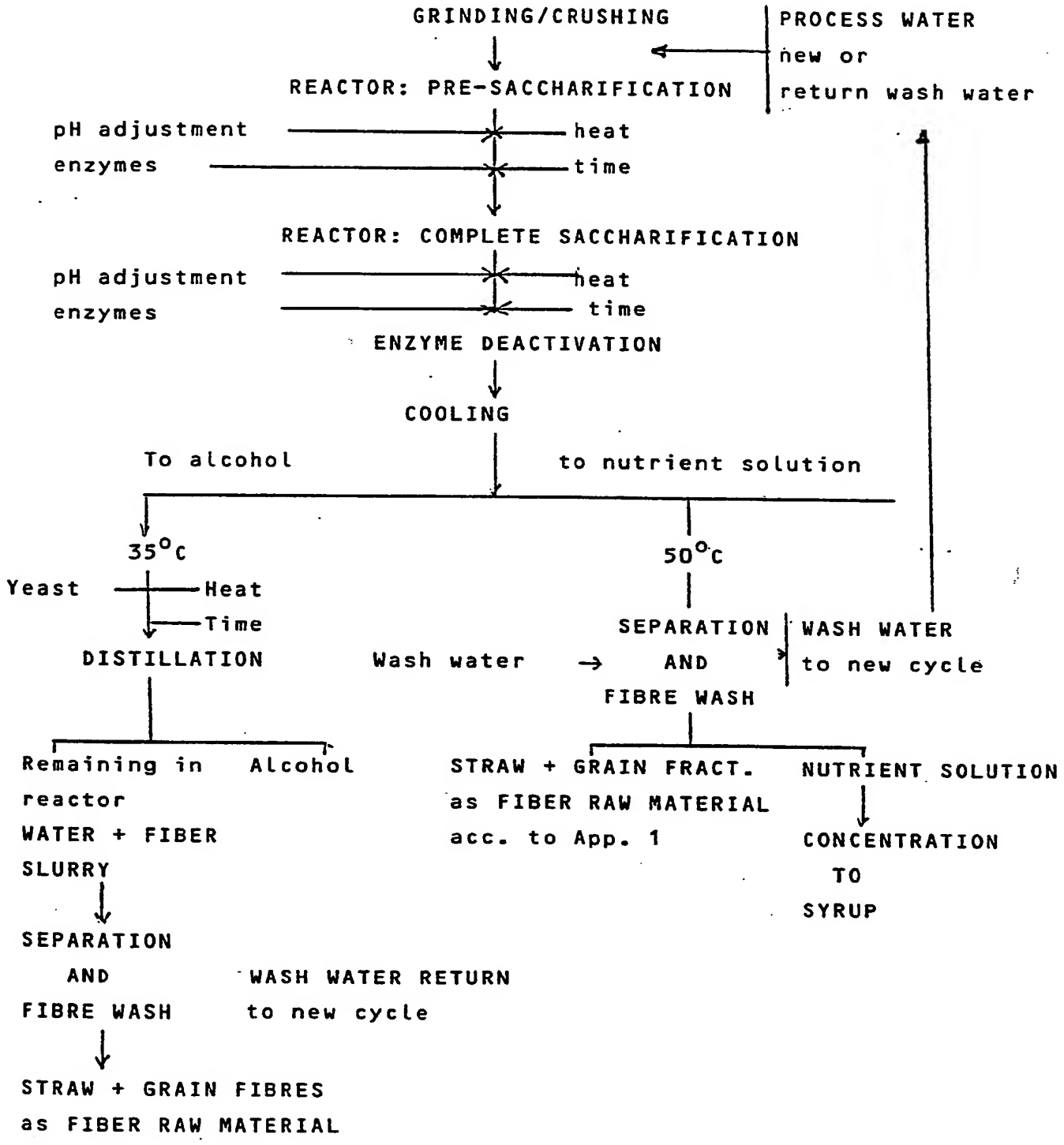
7. process for the preservation and moist storage of whole biomass, characterized in that calcium oxide powder is used in an amount of 2 to 5 % calculated on the whole biomass having a water content of 30 %.

Appendix 1.

FLOW DIAGRAM PULP SHEET



BIOMASS FROM WHOLE CEREALS (STRAW + GRAIN FRACTION)



Appendix 3.

RAW MATERIALS

Composition in % of DS

Wheat Straw		
Pure cellulose	32 %	27 to 37
Hemi cellulose	27	23 to 30
Lignine	21	19 to 24
Protein	3	2 to 4
Extractable compounds	10	7 to 12
Ashes	7	6 to 8
Total	100	
Husk of the wheat grain		
Pure cellulose	14 %	
Hemi cellulose	44	
Lignine	11	
Protein	15	
Extractable compounds	10	
Ashes	6	
Total	100	
The whole wheat grain		
Starch + sugar compounds	67	
Protein Nx6.25	15	
Husks	13	
Germs + fat	2	
Ashes	4	
Total	100	acc. Appendix 1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00169

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: D 21 C 3/02, C 12 P 7/10, C 12 S 3/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	D 21 C; C 12 P

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	SE, C, 137176 (E. ÖMAN) 2 September 1952, see page 1, column 1, line 32 - column 2, line 78	1,2,3
Y	--	4,5,6
X	GB, A, 312634 (EUROMERICAN CELLULOSE PRODUCTS CORPORATION) 27 March 1930, see page 1, column 2, line 86 - page 2, column 1, line 27	1,3
Y	--	4,5,6
X	GB, A, 834006 (THE BRITISH PAPER AND BOARD INDUSTRY RESEARCH ASSOCIATION) 4 May 1960, see page 1, column 1, line 10 - line 16; page 1, column 1, line 80 - column 2, line 62; page 2, column 2, line 80 - line 110	1,2,3
Y	--	4,5,6

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
5th June 1990	1990 -06- 12 12 JUL 1990
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Marianne Bratsberg

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	SE, B, 430792 (BIO RESEARCH CENTER CO LTD) 12 December 1983, see the whole document --	4,5,6
A	DE, A1, 3225074 (JOSEF ERNE & CO ROHRBOGENWERK) 12 January 1984, see the whole document --	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. [X] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. [ ] Claim numbers....., because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claim numbers....7..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The invention according to claim 7 is not described in the description in such a way that a meaningful search can be carried out.

3. [ ] Claim numbers....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. [X] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1) Claim 1 relates to a process for the manufacture of a cellulose-containing product.

2) Claim 7 relates to the preservation and storing of biomass.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the the claims. It is covered by claim numbers:

4. [X] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additonal fee.

Remark on Protest

[ ] The additional search fees were accompanied by applicant's protest.

[ ] No protest accompanied the payment of additional seach fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 90/00169

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 90-05-07 The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
SE-C- 137176	52-09-02	NONE		
GB-A- 312634	30-03-27	NONE		
GB-A- 834006	60-05-04	BE-A-	557608	00-00-00
		FR-A-	1175629	00-00-00
		NL-A-	217392	00-00-00
SE-B- 430792	83-12-12	BE-A-	833458	76-03-16
		CA-A-	1055861	79-06-05
		DE-A-B-C	2541960	76-04-08
		FR-A-B-	2285455	76-04-16
		GB-A-	1488318	77-10-12
		JP-C-	1224414	84-08-15
		JP-A-	51035484	76-03-25
		JP-B-	58039517	83-08-30
		NL-A-	7510948	76-03-23
		SE-A-	7510457	76-03-22
		US-A-	3990944	76-11-09
DE-A1- 3225074	84-01-12	EP-A-B-	0098490	84-01-18